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## Assessment of Pollution Status around 'Awosuuru' Dump-Site, Osogbo, Nigeria.

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### Abstract

The physicochemical properties with their distribution pattern and sources of sixteen polycyclic aromatic hydrocarbons (PAHs) listed as priority pollutants were investigated in underground water, sediment and soil samples around 'Awosuuru' dump-site in Osogbo Nigeria. The physicochemical parameters; degree of acidity (pH), total organic carbon (TOC), Biochemical oxygen demand (BOD), and chemical oxygen demand (COD), in the samples were determined using standard methods. The polycyclic aromatic hydrocarbons (PAHs) were analyzed quantitatively and qualitatively in the samples using gas chromatography coupled with flame ionisation detector (GC-FID). The values of pH and TOC ranged from 7.76 to 8.02 and 0.82 to 1.01 (wt%) in water; 7.70 to 8.34 and 0.35 to 1.17(wt%) in sediment; 8.03 to 8.56 and 0.51 to 1.05 (wt%) in soil respectively, BOD ranged from 0.02 to 0.07 (mg/L) and COD from 36.40 to 64.40 (mg/L) in water samples. The physicochemical parameters result showed that the samples have some amount of carbonates, biodegradable and oxidizable pollutants and organic matter reflecting pollution in the study area. The concentrations of PAHs recorded in the samples indicated moderate pollution. Various diagnostic PAHs ratios indicate pyrolytic source majorly from burning of refuse. Also, the health implication of the pollution status of the study area was discussed.

**Keywords:** Dumpsites, GC- FID, PAHs, pollution, TOC

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### Introduction

Environmental Pollution has become an increasing economic and social problem for many communities around the world. Pollution is associated with the introduction of chemical compounds, solid wastes, industrial discharge, human and animal wastes and other classes of contaminants directly or indirectly into the environment, resulting in harmful effect of such a nature as to endangered human health, harms

living resources and interferes with other legitimate use of the environment (Amokaye, 2012). Pollutant levels become unacceptable when they result in detrimental changes to an organism or the biological community (Kruczynski, 2002). The greatest danger to the quality of our environment is posed by human activities. Man in search for development and development and comfort has launched into industrial revolution

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had resulted in the development of various industrial sectors. The development of various industries and urbanization are accompanied by the introduction of different classes of contaminants into the environment (air, water and soil) which seriously damaging its natural processes (Solomon *et al.*, 2007). Environmental pollution due to the inability to manage increasing wastes generated from industries, urbanization, exploration of natural resources and modern agricultural practices is a major concern in most developing countries including Nigeria (McMichael, 2000). In highly populated cities rapid urbanization lead to increasing indiscriminate discharge of sewage and solid wastes (Saad *et al.*, 1994; Adekola *et al.*, 2003; Midodo and Orosanya, 2006). Most cities lack proper waste disposal facilities, heaps and accumulation of waste are seen in streets and open dumpsites (Ngigwe, 2008). Water bodies are one of the highly polluted environmental media (Adeyemo, 2003), water bodies are polluted due to runoff of these wastes into the water bodies, leaching of pollutant into groundwater and discharge of industrial effluents into the water bodies. The quality of any water body is governed by its physicochemical parameters. Water quality monitoring has a high priority for the determination of current conditions and long term trends for effective management of water bodies (Arian *et al.*, 2008). The assessment of physicochemical characteristics of water body is vital for both long term and short time evaluation of its quality. Physicochemical parameters such as Dissolved oxygen (DO) determination help to assess the raw water quality and to keep check on stream pollution.

Dissolved Oxygen, DO is the basis of Biochemical oxygen demand, BOD which is an important parameter in evaluating the pollution potential of domestic and industrial wastes. This might be due to the use of chemicals which are organic or inorganic and are oxygen demand (DWARF, 1996). The chemical oxygen demand (COD) is a measure of the oxygen equivalent of that portion of organic matter in a sample that is susceptible to oxidation by a strong chemical

oxidant (strong oxidising agents). High COD levels indicate toxic state of the waste waters along with presence of biologically resistant organic substances (Sawyer and McCarty, 1998).

Persistent organic and inorganic pollutants including Polyaromatic hydrocarbons, phthalate esters, pesticides and polychlorinated biphenyls and heavy metals have also been detected in water samples. Polycyclic aromatic hydrocarbons (PAHs) are known to enter environments through industrial discharges, petroleum spills, combustion of fuels, automobile exhausts, and non-point sources such as urban run-off and atmospheric fall out (Chen *et al.*, 2004; Yang *et al.*, 2014). They are neutral, non-polar, organic molecules which consist of two or more condensed benzene rings interconnected in different combinations with hydrophobicity which increases with the molecular weight. PAHs of petrogenic origin, prevalent in coals and fossil fuels, are formed from diagenesis of sedimentary organic material under low to moderate temperature and tend to consist of low molecular-weight PAHs with two to three aromatic rings while the pyrolytic PAHs consist mainly of four or more aromatic rings. The aim of this study is to determine some physicochemical parameters and level of polycyclic aromatic hydrocarbons (PAHs) in water, sediment and soil around Awosuuru dumpsite in Osogbo, Nigeria and to evaluate the associated health risk.

## Materials and Methods

### Study Area and Sample collection

'Awosur' dumpsite is located in Osogbo, southwest Nigeria. It is located about 300 m to the main road in Awosuuru along Iwo - Osogbo Road, Figure 1 show the location of the dumpsite. It is an open dumpsite receiving most of the solid waste within the area. Waste are dumped in the site without proper treatment and burnt. A stream flows beside the dumpsite transporting the solid dumps and leachates from the dumpsites to the surface water bodies and soil around the area. Soil, water and sediments samples were collected around the 'Awosuru' dumpsite located in Osogbo Nigeria. The sampling point coordinates

are as shown in table 1. Surface layer of soil samples (1-10 cm) and the stream sediment samples were collected from the dumpsite area. Samples were hand dug with a hand trowel that was cleaned prior to use and between samples.

The soil and stream sediment samples were collected into metal plates lined with aluminium foil. Water samples were collected into 250 ml amber bottles and were stored in the refrigerator at 4 °C before analysis. The soil and sediment samples were air dried and sieved with a sieve of 200 µm openings and stored in amber bottles.

### Determination of Water physicochemical Parameters

The dissolved oxygen content of the water samples were determined before and after five days incubation at 20 °C. The BOD is calculated on the basis of oxygen depleted. The pH of the samples was determined in-situ using the pH meter with digital voltmeter scale for direct pH measurement. The total organic carbon (TOC) was determined using Walkley-Black procedure (Walkley-Black 1934).

### Analysis of PAHs

10g each of sample (soil and sediments) was weighed with 10 g each of anhydrous sodium sulphate and grounded into free flowing powder.

Each sample was ultrasonically extracted with 30ml acetone-hexane (1:1, V/V) for 20 min. 200 ml of the water sample was transferred into a 1 L separating funnel and 60 ml of the redistilled dichloromethane was added. The separating funnel was shaken vigorously for about 2 min. with periodic venting to release vapour pressure. The organic layer was allowed to separate for 10 min .and was recovered into 250 ml flask. The aqueous layer was re-extracted twice with 60 ml of redistilled dichloromethane. The combined extract was dried by passing through the funnel containing the anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas. The concentrated extract was cleaned up in a column (30 cm x 10 mm i.d.) packed with silica gel/alumina (4:1). The column was pre-eluted with 30 ml of hexane before loading the sample. The concentrated extract was separated into saturate, aromatic (PAHs) and polar fractions by using 30 ml of n- hexane, 30 ml of n- hexane / dichloromethane (2:3,v/v) and 30 ml of methanol respectively. The PAH fraction was subjected to gas chromatographic analysis. Aliquot of PAH fraction was injected into a gas chromatography HP 5890 powered with HPCMEM software with flame ionization detector (FID). The separation was effected on 30 cm x 0.25 mm i.d., HP-5 fused silica column using nitrogen as carrier gas. The oven temperature ramped at 100 °C (2 min hold)

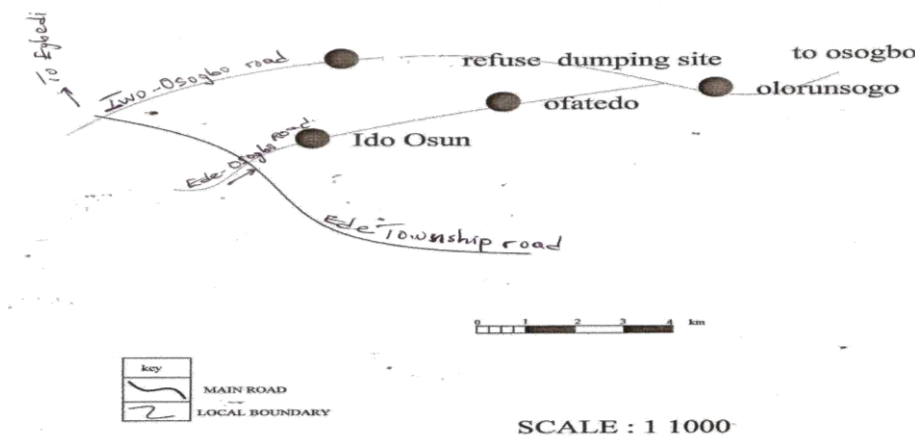


Figure 1: Awosuuru Dumpsite showing soil sampling sites

followed by 280 °C for 16 min at 10 °C/min, then 300 °C for 4 min and 10 °C/min. The USEPA 16 priority PAHs standard mix was analyzed using the same instrumental conditions. The identification of PAHs was by comparison of samples retention times with that of the USEPA standard mix. The quantification was performed using external calibration method based on five point's calibration curves for the standard PAHs mix.

For quality control, all solvents used for the analysis were high purity analytical grade, recovery studies was carried out by spiking samples of known concentration of PAHs with PAH mix standard of known concentrations and analysed by the test method. Two methods blanks (solvents) were also analysed along with the field samples. The concentrations of the PAHs in the method blanks are below the method detection limit.

#### Data Analysis

The concentration of the PAHs in the soil and sediments samples were presented based on the dry weight equivalent of the samples. The total concentration of the PAHs are based on the sum of the sixteen United State Environmental Protection Agency, USEPA priority PAHs. To assess the potential ecotoxicity and health risk due to the presence of PAHs in the soil, water and sediments samples, the percentage concentration of carcinogenic and mutagenic PAHs were calculated from the average concentrations of individual PAHs from each sample. The carcinogenic and mutagenic potency were also calculated by multiplying the average concentration of PAHs with the Bap-toxicity equivalent factors and with Bap-mutagenic equivalent factors proposed by Nisbet and Lagoy, 1992; Busby *et al.*, 1996). Diagnostic ratios of PAHs are employed to identify the sources of the PAHs in the samples, the values of anthracene /anthracene+phenanthrene, ( $\text{Ant}/(\text{Ant}+\text{Phe})$ ), phenanthrene/anthracene, ( $\text{Phe}/\text{Ant}$ ), fluoranthene/pyrene ( $\text{Flu}/\text{Pyr}$ ) and Benzo(a)pyrene/(Benzo(a)pyrene + chrysene) ratio

have been used extensively to distinguish between petroleum and combustion sources of PAHs. The value of Phe/Ant greater than 10 and Flu/pyr less than 1 suggest petrogenic origin and value between 1.0 - 1.4 indicates biomass and coal combustion source, Ant/(Ant+Phe) less than 1 is an indication of petroleum origin while less than 0.1 indicates combustion source (Yunker *et al.*, 2002; Huang *et al.*, 2003). Also, the value of Flu/(Flu+Pyr) less than 0.4 indicates petrogenic source, and 0.4- 0.5 pyrogenic source and greater than 0.5 indicates combustion of biomass (Yunker *et al.*, 2002; Chen *et al.*, 2005). Furthermore, benzo(a)anthracene/(benzo(a)anthracene + chrysene)( $\text{BaA}/(\text{BaA} + \text{Chr})$ ) of 0.35 and ideno(123-cd)pyrene/ideno(123-cd) pyrene + benzo(ghi)perylene ( $\text{Icdp}/(\text{Icdp} + \text{Bghip})$ ) of 0.5 mark the transition point of the petroleum and combustion sources. Specifically,  $\text{BaA}/(\text{BaA} + \text{Chr}) < 0.2$ , between 0.2-0.35 and  $>0.35$  indicates mainly petroleum input, inputs from both sources and combustion input, respectively. Likewise,  $\text{Icdp}/(\text{Icdp} + \text{Bghip}) > 0.2$ , between 0.2-0.5 and more than 0.5 infers petroleum input, liquid fossil fuel combustion and grass, wood and coal combustion, respectively (Yunker *et al.*, 2002).

#### Results and discussion

##### Physicochemical parameters

The pH, total organic carbon, biochemical oxygen demand and chemical oxygen demand of the samples were determined, the results of the physicochemical parameters were presented in Table 1. The pH of the water samples ranged between 7.76 and 8.02 with a mean value of 7.88, soil between 8.02 and 8.56 and sediment between 7.70 - 8.12. the pH of an aquatic ecosystem is an important indicator of water quality, the pH of the water samples and the sediments shows alkalinity in its value. The mean pH value of the water samples is higher than the recommended pH range for portable water. The World Health organization, WHO acceptable pH value for portable water was 6.8 and 7.4 (DWARF, 1996; Akan *et al.*, 2008). The chemical oxygen demand is a measure of the oxygen equivalent of the organic

Table 1: Physicochemical parameters of the samples

Sample	Location	BOD (mg/L)	COD (mg/L)	pH	TOC (wt %)
OSw <sub>1</sub>	N 07° 46'.25 E 004° 32'.28	0.07±0.02	36.40±12.20	7.76±0.06	1.01±0.01
OSw <sub>2</sub>	N 07° 46'.26 E 004° 32'.29	0.06±0.015	64.40±10.59	7.85±0.05	0.97±0.07
OSw <sub>3</sub>	N 07° 46'.24 E 004° 32'.27	0.02±0.015	45.20±10.43	8.02±0.02	0.82±0.02
OSsoil <sub>1</sub>	N 07° 47'.60 E 004° 29'.35	ND	ND	8.03±0.03	1.05±0.03
OSsoil <sub>2</sub>	N 07° 47'.64 E 004° 29'.05	ND	ND	8.56±0.06	0.70±0.05
OSsoil <sub>3</sub>	N 07° 47'.61 E 004° 29'.65	ND	ND	8.34±0.04	0.51±0.02
OSsed <sub>1</sub>	N 07° 46'.25 E 004° 32'.28	ND	ND	7.70±0.10	0.35±0.35
OSsed <sub>2</sub>	N 07° 46'.26 E 004° 32'.29	ND	ND	7.85±0.05	0.86±0.86
OSsed <sub>3</sub>	N 07° 46'.24 E 004° 32'.27	ND	ND	8.12±0.02	1.17±1.17

OSw - Osogbo water sample; OSsoil - Osogbo soil; OSsed - Osogbo sediment; ND - Not Determined; BOD-Biochemical Oxygen Demand; COD-Chemical Oxygen Demand

Table 2.0 concentration of PAHs in soil, water and sediments (µg/kg)

PAH	OS soil <sub>1</sub>	OSsoil <sub>2</sub>	OSsoil <sub>3</sub>	OS sed <sub>1</sub>	OS sed <sub>2</sub>	OSsed <sub>3</sub>	OSw <sub>1</sub>	OSw <sub>2</sub>	OSw <sub>3</sub>
Naphthalene	0.1455	0.1462	0.1043	0.0641	0.0657	0.0745	0.0305	0.0241	0.0675
Acenaphthylene	2.3928	1.3777	1.7453	0.5538	0.7574	0.7294	0.9682	0.7554	0.8148
Acenaphthene	1.3264	1.3978	1.2146	0.5649	0.7167	0.7199	0.7129	0.5769	0.7516
Fluorene	2.5293	2.6516	1.7445	1.0730	1.8793	1.3661	0.7154	0.5620	0.6165
Phenanthrene	2.4430	2.5220	1.6293	1.0344	1.7978	1.2927	0.9010	0.7879	0.8036
Anthracene	1.3116	1.3665	1.0222	0.5580	0.5346	0.7165	0.9153	0.6877	0.8830
Fluoranthene	1.6634	1.6688	1.9763	0.6763	0.7119	0.8176	0.4842	0.4667	0.5811
Pyrene	0.9282	0.9288	0.8978	0.3992	0.3123	0.4839	0.9935	0.8967	0.6014
Benzo(a)anthracene	1.8332	1.8470	2.1148	0.8188	0.8012	0.9558	0.6496	0.8640	0.9691
Chrysene	1.4440	1.4675	1.6736	0.6341	0.6782	0.7479	0.2198	0.6182	0.6310
Benzo(b)fluoranthene	0.2158	0.8147	0.3748	0.0950	0.0188	0.1096	0.1121	0.0408	0.0435
Benzo(k)fluoranthene	0.0638	1.4324	0.5954	0.02947	0.0124	0.0348	0.0602	0.0238	0.0172
Benzo(a)pyrene	6.8832	16.9162	5.9521	2.9260	2.95186	3.5805	0.0021	0.0088	0.0230
Indeno(1,2,3-cd)pyrene	1.7966	1.8396	1.6159	0.8222	0.7648	0.9237	0.0034	0.0016	0.0049
Dibenzo(a,h)anthracene	0.7877	0.7517	0.3252	0.3620	0.1295	0.3596	0.0002	0.0004	0.0016
Benzo(g,h,i)Perylene	0.2301	0.2375	0.0825	0.1092	0.4527	0.1161	0.0002	0.0001	0.0010
Σ16EPA	25.9966	37.3660	23.0686	10.7204	12.5852	13.0286	6.7686	6.3151	6.8108
Mean	1.6248	1.7104	1.3931	0.6700	0.7866	0.8143	0.4230	0.4369	0.4257
ΣLMW PAH	10.1486	9.4618	7.4602	3.8482	5.7515	4.8991	4.2433	3.394	3.937
ΣHMW PAH	15.846	27.9042	15.6084	6.87227	6.83366	8.1295	2.5253	2.9211	2.8738

Σ16EPA = total concentration of 16 EPA PAHs; ΣLMW PAH = total concentration of low molecular weight PAHs, ΣHMWPAH = total concentration of high molecular weight PAHs.

matter content of the sample that is susceptible to oxidation by strong chemical oxidants. The value of the chemical oxygen demand of the water sample ranged between 36.40mg/L to 64.40mg/L. The COD values show that all the

water samples are polluted. The Total Organic Carbon, TOC value in the water samples ranged between 0.82 - 1.01, soil between 0.51 - 1.05 and sediments between 0.35 - 1.17. TOC values show that the samples contain significant amount of

organic pollutants one of which could be polycyclic aromatic hydrocarbons (Sunita and Sumanjeet 1999).

**Occurrence and Spatial Distribution of Polyaromatic hydrocarbons**

The concentrations of the 16 PAHs, sum of which is defined as  $\Sigma 16\text{PAHs}$  are presented in Table 2.0. The concentrations of the  $\Sigma 16\text{PAHs}$  in soil samples were the highest, the concentration

Of PAHs in the soil sample ranged from 23.068 $\mu\text{g}/\text{kg}$  to 37.366  $\mu\text{g}/\text{kg}$  with a highest mean concentration of 1.7104  $\mu\text{g}/\text{kg}$  (Table 2). Organic pollutants accumulates in the water sediments and the concentration of  $\Sigma 16\text{PAHs}$  in the sediment samples are higher than that of the water samples, the  $\Sigma 16\text{PAHs}$  in the sediment and water samples ranged from 10.7204  $\mu\text{g}/\text{kg}$  to 13.0286  $\mu\text{g}/\text{kg}$  and 6.3151  $\mu\text{g}/\text{kg}$  to 6.8108  $\mu\text{g}/\text{kg}$  respectively. The mean concentrations of the

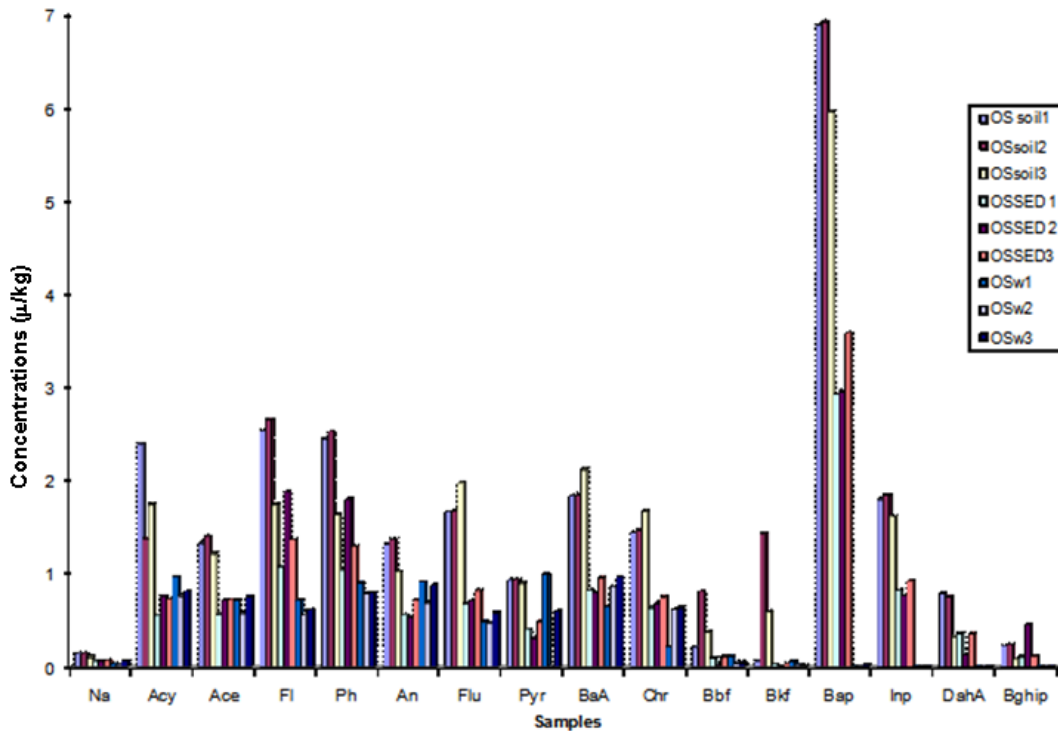


Figure 2: Distribution of individual PAHs at different locations

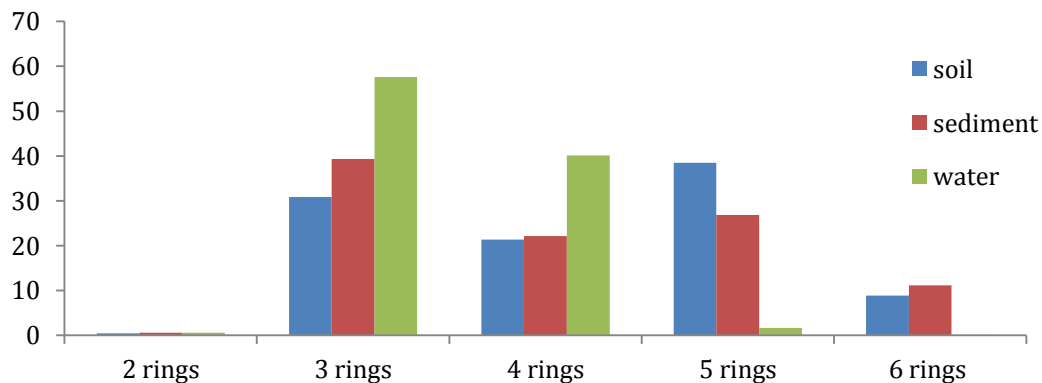


Figure 3: Percentage ring size distribution of PAHs in the soil, sediments and water samples

PAHs in the dumpsite soil are higher than that of the sediments and the surface water samples. The total concentration of high molecular weight PAHs,  $\Sigma$ HMPAHs in all the soil and sediments samples are higher than the total concentrations of the low molecular weight PAHs,  $\Sigma$ LMWPAHs, the percentage concentration of  $\Sigma$ LMWPAHs is 31.32 %, 39.91 % and 58.18 % in soil, sediment and water respectively and the percentage

concentration of  $\Sigma$ HMPAHs 68.86 %, 60.09 % and 58.18% respectively. A marked distribution pattern of the PAHs concentration in the samples was apparent, 1-,2-,3-,4-,5- and 6- ring size PAHs are detected in all the water, soil and sediments samples with predominance of 3-,5- and 4- ring size PAHs in the soil and sediment samples and predominance of 3- and 4- ring size PAHs in the water samples, the 3- and 4- rings size PAHs

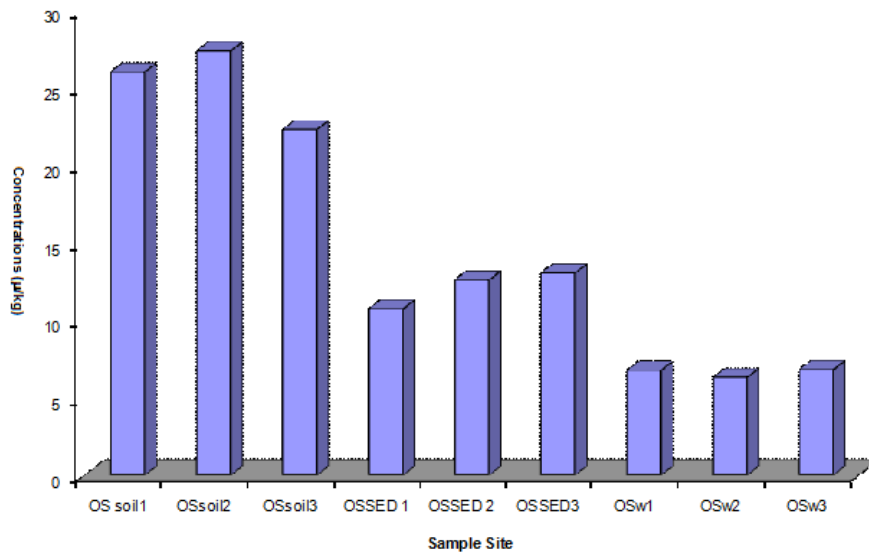


Figure 4: Relative distributions of PAHs at different locations

Table 3: Relative distribution pattern ( $\mu\text{g}/\text{kg}$ ) and percentage composition of individual PAHs in the samples

Samples	2 rings	3 rings	4 rings	5 rings	6 rings
<b>Soil</b>					
Os soil <sub>1</sub>	0.145480	8.00305	5.868733	1.06940	2.02669
Os soil <sub>2</sub>	0.146150	9.31548	5.912217	9.91502	2.07708
Os soil <sub>3</sub>	0.104338	7.35580	6.66220	7.24786	1.69828
Total	0.3960	24.6743	18.4426	18.2323	5.8021
<b>%</b>	<b>0.59</b>	<b>36.53</b>	<b>26.99</b>	<b>26.99</b>	<b>8.99</b>
<b>Sediment</b>					
Os sed <sub>1</sub>	0.0640867	3.28175	2.34701	0.17455	0.003523
Os sed <sub>2</sub>	0.065671	5.68579	2.84524	0.07383	0.001695
Os sed <sub>3</sub>	0.0744679	4.824664	2.78264	0.08527	0.00586
Total	0.2042	13.7922	7.9749	0.3337	0.0111
<b>%</b>	<b>0.59</b>	<b>40.03</b>	<b>40.12</b>	<b>1.68</b>	<b>0.06</b>
<b>Water</b>					
Os w <sub>1</sub>	0.0304759	4.21281	2.34701	0.17455	0.003523
Os w <sub>2</sub>	0.0240628	3.35397	2.84524	0.07383	0.001696
Os w <sub>3</sub>	0.674808	3.8695	2.78264	0.08527	0.00586
Total	0.1220	11.4363	7.9749	0.3337	0.0111
<b>%</b>	<b>0.61</b>	<b>57.53</b>	<b>40.12</b>	<b>1.68</b>	<b>0.06</b>

accounted for approximately 57.56 % and 40.09 % of the  $\Sigma 16$ PAHs in all the water samples (figure 2). The 5-rings PAHs accounted for 38.47%, 26.85% and the 3-rings PAHs 30.86 %, 39.34 % of the  $\Sigma 16$ PAHs in the soils and sediments samples respectively. The levels of  $\Sigma 16$  PAHs in the soil and sediment samples are lower than those reported for soils from other parts of the world (Table 4) (Sojину *et al.*, 2010). The total concentrations of Beijing urban soil ranged from 467 to 5,470  $\mu\text{g}/\text{kg}$  and also five cities (Tallinn, Helsinki, Vilnius, Chicago, and London) urban soils had a concentration of 1090  $\mu\text{g}/\text{kg}$  (mean value). For sediment, the total concentration of England and Wales is 102,000  $\mu\text{g}/\text{kg}$ . While for water, the total concentration of PAH in yellow river, China, ranged from 31  $\mu\text{g}/\text{kg}$  to 133  $\mu\text{g}/\text{kg}$ . For water samples, comparison of the concentration of some PAHs in the study area with the Canadian and Netherlands guidelines for water analysis shows that the water samples under study are polluted (Table 5).

### Source Diagnostic Ratios

The source diagnostic indices are calculated from interpretative PAH concentrations and presented in Tables 6. The values of these ratios were used to indicate source of the PAHs (Sojину *et al.*, 2010; Adedosu *et al.*, 2013). The *Ph/An* ratio ranged from 0.91 to 1.15, 1.80 to 3.36 and 1.59 to 1.86 in water, sediment and soil respectively, this values are less than 10 and indicates pyrogenic sources of PAHs in the samples (Adedosu *et al.*, 2013). The value of the *Flu/Pyr* ratio ranged from 0.61 to 1.03, 2.69 to 6.02 and 1.94 to 2.86 in water, sediment and soil respectively. This value suggested a pyrogenic source of PAHs mostly from combustion of biomass and *Bap/Chr* ratios ranged from 1.40 to 2.96, 1.18 to 1.28 and 1.26 to 1.27 in water, sediment and soil respectively. These ratios are higher than 1 but lesser than 10 in all the samples, therefore indicating pyrolytic source. The range of values of *Nap /Ace, An/ Ph + An, Flu/Flu + Pyr, BaA/BaA + Chr and InP /InP + Bghip* are lesser than 1 in all the samples thus indicating pyrolytic source.

Table 4: Global distribution of Polycyclic aromatic hydrocarbons in soils and sediments (Sojину *et al.*, 2010)

Location	No of PAHs	PAHs ( $\mu\text{g}/\text{kg}$ )	Source type
<b>Soils</b>			
Beijing, China	16 EPA	467-5,470	Urban soils
Canada	17	1,400	Highway
U.K	07	20,000	Motorway
U.S	14	3,000	Highway
Australia	18	300-79,000	Chemical plant
Japan	08	1300 <sup>a</sup>	Urban soils
U.K.	16	2,700 <sup>a</sup>	Urban soils
New Orleans (U.S)	16	3,730	Urban soils
W. Macedonian (Greece)	16	55.2-495	Lignite fire plant
Linz(Austria)	18	1450 <sup>a</sup>	Industrial area
Zeizate(Belgium)	07	3,000-14,000	1.3-4.2km from an Oil refinery
Five cities (Tallinn, Helsinki, Vilnius, Chicago& London)	16	1,090 <sup>a</sup>	Urban soils
Novi Sad (Serbia & Montenegro)	16	47,900 <sup>a</sup>	Oil refinery
Tokushima (Japan)	13	611 <sup>a</sup>	Urban soils
Niger Delta, Nigeria	28	23.8-120	Close to oil Installations
<b>Sediments</b>			
England & Wales	16EPA	102,000	Surface
Thailand	14	6-8,400	Surface
Yellow river, China	13	31-133	Surface
Niger Delta, Nigeria	28	65-331	Close to oil installations

<sup>a</sup> Mean values

Table 5: Comparison of the Concentration of some Selected PAHs in water samples from the Study Area with the Canadian and Netherlands Guidelines for water analysis ( $\mu\text{g}/\text{kg}$ )

PAHs	Mean Concentration	Canadian (2008) mean concentration	Netherlands(2008) mean concentration
Nap	0.0467	0.00011	NA
Ace	0.6804	0.00058	0.0012
Flu	0.0300	0.0003	0.00007
Ant	0.8287	0.000012	0.00007
Phe	0.0300	0.0004	0.0003
Fla	0.5107	0.00004	0.0003
Pyr	0.8306	0.000025	NA
Chr	0.0300	NA	0.00034
B[a]A	0.0300	0.000018	0.00001
B[a]P	0.0300	0.000015	0.00005
Bkf	0.0337	NA	0.00004
B[ghi]P	NA	0.000033	0.00006

NA: Not Available

Table 6: Molecular indices of PAHs in the samples

Sample	Ph/An	Flu/Pyr	Bap/Chr	Nap/Ace	An/(Ph+An)	Flu/(Flu + Ph)	BaA/(BaA+ Chr)	InP/(Inp + Bghip)
OSsoil <sub>1</sub>	1.86	2.73	1.27	0.11	0.35	0.64	0.56	0.89
OSsoil <sub>2</sub>	1.85	2.86	1.26	0.11	0.35	0.64	0.56	0.99
OSsoil <sub>3</sub>	1.59	1.94	1.26	0.86	0.39	0.69	0.56	0.95
OSsed <sub>1</sub>	1.85	2.69	1.29	0.11	0.35	0.63	0.56	0.88
OSsed <sub>2</sub>	3.36	6.02	1.18	0.09	0.23	0.70	0.54	0.63
OSsed <sub>3</sub>	1.80	2.82	1.28	0.10	0.36	0.63	0.56	0.89
OSw <sub>1</sub>	0.98	0.72	2.96	0.04	0.50	0.03	0.75	0.96
OSw <sub>2</sub>	1.15	0.61	1.40	0.04	0.47	0.34	0.58	0.80
OSw <sub>3</sub>	0.91	1.03	1.54	0.09	0.92	0.88	0.61	0.84

### Carcinogenic and Mutagenic Potency of PAHs

The main concerns about the environmental contamination by PAHs are due to their health effect on human and other animals. Some of the polycyclic aromatic hydrocarbons are known human carcinogens and mutagens, Glower (1990) reported the mutagenic potential of Dibenzo(a,h)anthracene, benzo(a)pyrene and benzo(g,h,i)pyrene. The international Agency for research on cancer, IARC have also listed chrysenes, benzo(a)anthracene, Dibenzo(a,h)anthracene, benzo(a)pyrene, benzo(b)fluoranthrene, benzo(k)fluoranthrene and indeo(1,2,3-cd)pyrene are potential human carcinogen (WHO, 1998, USEPA, 2012). All the listed carcinogenic and mutagenic PAHs are detected in the soil, water and sediment samples

collected around the dumpsite. Table 7.0 shows the concentration of carcinogenic and mutagenic PAHs in the soil, water and sediment samples, the mean concentration of benzo(a)pyrene, a carcinogenic and mutagenic PAHs is highest in the soil sample ( $9.92\mu\text{g}/\text{Kg}$ ) and sediment ( $3.15\mu\text{g}/\text{Kg}$ ), the total mean concentration of carcinogenic PAHs in the soil, sediments and water samples are  $10.72\mu\text{g}/\text{Kg}$ ,  $3.66\mu\text{g}/\text{Kg}$  and  $0.013\mu\text{g}/\text{Kg}$  respectively. To assess the ecotoxicology risks at a particular site, the Benzo(a)pyrene-equivalent carcinogenicity and mutagenicity of the PAHs in the soil, sediments and water samples were calculated, the Bap-TEQ (carcinogenic equivalent) and Bap-MEQ (mutagenic equivalent) were calculated by multiplying the concentration of each PAHs compound with its TEF for cancer relative to Bap (Nisbet and LaGoy, 1992)

Table 7.0: carcinogenic and mutagenic potency of PAHs in the soil, sediments and water samples

PAHs	Mean concentration of carcinogenic PAHs (mg/kg)	TEF	B[a]P-TPE	MEF	B[a]P-MEQ
<b>Soil sample</b>					
Benzo(a)anthracene	1.93	0.1	0.193	1.5826	1.5826
Chrysene	1.53	0.01	0.015	0.02601	0.0260
Benzo(k)fluoranthene	0.47	0.1	0.047	0.1175	0.1175
Benzo(b)fluoranthene	0.70	0.1	0.070	0.077	0.0770
Benzo(a)pyrene	9.92	1	9.920	9.92	9.9200
Indeno(1,2,3cd)pyrene	1.75	0.1	0.175	0.5425	0.5425
Dibenzo(ah)anthracene	0.62	5	3.100	0.1798	0.1798
Benzo(g,h,i)pyrene	0.18	0.01	0.0018	0.0342	0.0342
ΣCPAH	16.92	-			
ΣMPAH	10.72				
%CPAH	65				
<b>Sediment sample</b>					
Benzo(a)anthracene	0.87	0.1	0.087	1.5826	0.7134
Chrysene	0.69	0.01	0.007	0.02601	0.01173
Benzo(k)fluoranthene	0.07	0.1	0.007	0.1175	0.0175
Benzo(b)fluoranthene	0.03	0.1	0.003	0.077	0.0033
Benzo(a)pyrene	3.15	1	3.150	9.92	3.15
Indeno(1,2,3cd)pyrene	0.84	0.1	0.084	0.5425	0.2604
Dibenzo(ah)anthracene	0.29	5	1.450	0.1798	0.0841
Benzo(g,h,i)pyrene	0.23	0.01	0.0023	0.0342	0.0437
ΣCPAH	5.92				
ΣMPAH	3.66				
%CPAHs	15.83				
<b>Water sample</b>					
Benzo(a)anthracene	0.83	0.1	0.083	1.5826	0.6806
Chrysene	0.50	0.01	0.005	0.02601	0.0085
Benzo(k)fluoranthene	0.07	0.1	0.007	0.1175	0.0175
Benzo(b)fluoranthene	0.04	0.1	0.004	0.077	0.0044
Benzo(a)pyrene	0.01	1	0.01	9.92	0.01
Indeno(1,2,3cd)pyrene	0.01	0.1	0.001	0.5425	0.0031
Dibenzo(ah)anthracene	0.001	5	0.005	0.1798	0.00029
Benzo(g,h,i)pyrene	0.0004	0.01	0.000004	0.0342	0.000076
ΣCPAH	1.432				
ΣMPAH	0.013				
%CPAHs	6.21				

and MEF relative to Bap (Busby *et al.*, 1996; Durant *et al.*, 1999). The Bap-MEQ and Bap-TEQ are shown in table 7.0. the Bap-TEQ and Bap-MEQ values for benzo(a)anthracene, dibenzo(a,h)anthracene and Benzo(a)pyrene are the highest in the soil and sediments samples and are the most toxic when compared with other carcinogenic and mutagenic PAHs.

### Conclusion

The results of the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of water samples, the pH and total organic carbon of all the samples showed that all the samples have some amount of carbonates, biodegradable and oxidizable pollutants and organic matter indicating pollution in the study area. The area under study is also moderately polluted based on the concentration of PAHs in the soil, sediment and water samples and potential source of PAHs contamination is pyrolytic, which result from majorly burning of refuse. The dumpsite constitutes a health risk for the people living within the vicinity of the dumpsite due to the accumulation of carcinogenic PAHs in the dumpsite soil which could leach to groundwater and runoff into nearby surface water bodies around the area. Therefore, it is recommended that an improved waste management system should be established.

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